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(54) A molded antimicrobial article and a process for its production

(57) A molded antimicrobial article comprises an infiltrated antimicrobial agent which forms independent phases of 0.01 μm or more in shorter diameter in the molded article. It is preferable that the antimicrobial agent is a pyridine based antimicrobial agent with a molecular weight of 200 to 700 and an inorganic property/organic property value of 0.3 to 1, and that 50% or more of the antimicrobial agent is infiltrated in a depth range of 0.5, preferably, 1 μm or more from the surface of the molded article, or that 30% or more of the antimicrobial agent is infiltrated in a depth range of 2 μm or more from the surface of the molded article. It is also preferable that the molded article is fibers, that the surface area used per 1 g of fibers is 0.1 m^2 or more, and that the synthetic fibers are a colored antimicrobial fibrous product.

The molded antimicrobial article of the present invention can be obtained, for example, by immersing a fibrous product in a dyeing liquid containing a pyridine based antimicrobial agent with a molecular weight of 200 to 700, an inorganic property/organic property value of 0.3 to 1.4 and an average particle size of 2 μm or less, and treating simultaneously with dyeing under pressurization, or by applying a liquid containing a pyridine based antimicrobial agent with a molecular weight of 200 to 700, an inorganic property/organic property value of 0.3 to 1.4 and an average particle size of 2 μm or less to a fibrous product by padding or spraying, and heat-treating it at 160 to 200°C in dry or wet state.

EP 0 952 248 A2

Description

Technical Field

[0001] The present invention relates to a molded antimicrobial article, particularly antimicrobial fibers excellent in industrial washing durability, and a production process thereof.

Prior Art

[0002] Molded antimicrobial articles, especially fibers are widely used for various clothes, interlinings, linings, bedclothes, interior products, etc. These fibrous products are excellent in antimicrobial activity and have become very high in water washing durability at households by various improvements.

[0003] However, in recent years, the hospital infection due to methicillin resistant Staphylococcus (MRSA) poses a problem. As a countermeasure, white overalls, covers, sheets, curtains, etc. must be treated to be antimicrobial. However, these fibrous products of hospitals are usually very frequently industrially washed at 60 to 85°C, and few of conventional techniques can provide sufficient durability against such washing.

[0004] Fibers can be treated to be antimicrobial by blending an inorganic antimicrobial agent such as silver, copper or zinc into synthetic fibers in the stage of spinning, or by applying an organic antimicrobial agent such as a quaternary ammonium salt by spraying or padding as post-treatment. The former method is excellent in view of washing durability, but does not allow antimicrobial treatment in a later stage. Furthermore, the antimicrobial agent is precipitated as crystal on the spinneret face in the stage of spinning, to cause frequent fiber breaking, etc. as a problem in the yarn production process. On the other hand, the latter method is poor in the washing durability of the antimicrobial activity though advantageously allows antimicrobial treatment in a later stage.

[0005] JP-A-61-239082 describes a case of treating N6 socks in a pyridine based antimicrobial agent suspension at 130°C for 60 minutes with shaking, but when a suspension is used, the particle size of the antimicrobial agent is too large to obtain a sufficient effect. Furthermore, JP-A-09-273073 describes a case of treating polyester fibers by a pyridine based antimicrobial agent simultaneously with dyeing, but the antimicrobial agent used is not proper and does not provide a sufficient effect.

Problem to Be Solved by the Invention

[0006] In view of the prior art, the present invention provides a molded antimicrobial fibrous product excellent in industrial washing durability and a production process thereof.

Means for solving the problem

[0007] The present invention relates to a molded antimicrobial article, comprising an infiltrated antimicrobial agent which forms independent phases of 0.01 μm or more in shorter diameter in the molded article. It is preferable that a pyridine based antimicrobial agent with a molecular weight of 200 to 700 and an inorganic property/organic property value of 0.3 to 1.4 forms independent phases of 0.01 μmor more in shorter diameter in the molded article, and that 50% or more of the antimicrobial agent is infiltrated in a depth range of 0.5, preferably, 1 μm or more from the surfaces of fibers, or 30% or more of the antimicrobial agent is infiltrated in a depth range of 2 μm or more from the surfaces of fibers. It is also preferable that the molded article is fibers, that the surface area used per 1 g of fibers is 0.1 m^2 or more, and that the synthetic fibers are a colored antimicrobial fibrous product.

[0008] The molded antimicrobial article of the present invention can be obtained, for example, by immersing a fibrous product in a dyeing liquid containing a pyridine based antimicrobial agent with a molecular weight of 200 to 700, an inorganic property/organic property value of 0.3 to 1.4 and an average particle size of 2 μm or less, and, preferably, treating simultaneously with dyeing under pressurization.

[0009] As another embodiment, the antimicrobial article can be obtained also by applying a liquid containing the same pyridine based antimicrobial agent to a fibrous product by padding or spraying, and heat-treating it at 160 to 200°C in dry or wet state.

Preferable Embodiments

[0010] A preferable antimicrobial agent used in the present invention has a molecular weight of 200 to 700, an inorganic property/organic property value of 0.3 to 1.4 and an average particle size of 2 μm or less.

[0011] A pyridine based antimicrobial agent is stably infiltrated and diffused in a molded article, especially synthetic fibers and a synthetic resin film. The molded article can also be of any other form such as a film, sheet, plate or rod,

but since the explanation becomes too complicated, cases of fibers are described below for the sake of convenience in this specification. It can be considered that if the antimicrobial agent is made closer in three requirements of molecular weight, inorganic property/organic property value and average particle size, to the disperse dye to be infiltrated and dispersed in the molded article, it shows behavior similar to that of the disperse dye.

[0012] However, it is surprising that the solid antimicrobial agent forms independent phases of 0.01 μm or more in shorter diameter (this means number average diameter of width direction of the phases in the cross-section) inside the fibers, and that 50% or more of it is infiltrated in a depth range of 0.5, preferably, 1 μm or more from the surfaces of fibers or that 30% or more of it is infiltrated in a depth range of 2 μm or more from the surfaces of fibers. Since it is hard to think that the antimicrobial agent is diffused as particles in the highly crystalline and structurally dense fibers, it is considered that it is dispersed as respectively single molecules or groups consisting of several cohesive molecules, to be precipitated which forms independent phases in the fibers. As for the diffusion degree of the antimicrobial agent, if the distance from the fiber surface to the center of the fiber section is 1, it is infiltrated and diffused to at least a distance of 0.2, and as for the concentration distribution of the antimicrobial agent in this case, the ratio of the concentration of the antimicrobial agent existing in a range from the center of the fiber section to a distance nearest to the center of the fiber section to the concentration of the antimicrobial agent existing in a range from it to the surface layer is 1 : 1 to 1 : 10. So, the antimicrobial agent is sufficiently infiltrated inside the fibers. Unless these conditions are satisfied, the antimicrobial agent is not infiltrated to be diffused in the synthetic fibers, and sufficient industrial washing durability cannot be obtained.

[0013] If the molecular weight is less than 200, washing durability is low, though the antimicrobial agent is infiltrated and diffused in the synthetic fibers. On the other hand, if the molecular weight is more than 700, the antimicrobial agent is not infiltrated in the synthetic fibers. It is preferable that the molecular weight of the antimicrobial agent is 300 to 500.

[0014] The "inorganic property/organic property value" referred to in the present invention is a value devised by Minoru Fujita for expressing the polarity of various organic materials as an organic idea [Revised Edition, Science of Chemical Experiments - Organic Chemistry - Kawade Shobo (1971)]. It is a ratio of the sum of inorganic property values to the sum of organic property values obtained from the inorganic property values and organic property values of various polar groups decided as shown in Table 1 with the organic property value of one carbon atom as 20.

Table 1

Inorganic group	Value
Light metal salt	>500
Light metal salt, amine or ammonium salt	>400
$-ASO_3H$, $-AOS_2H$	300
$-So_2NHCO-$, $-N=N-NH_2$	260
$-SO_3H$, -CONHCONHCO-	250
$-SO_2NH-$, -CONHCONH-	240
-CONHCO-, -CSNH-	230
=NOH	220
=N-NH-	210
-CONH-	200
-CSSH	180
-CSOH, -COSH	160
Anthracene nucleus or phenanthrene nucleus	155
-COOH	150
Lactone	120
-CO-O-CO-	110
-OH,-As-O-As-	100
-Hg (organic)	95
-COSR, -CSOR, -AS=AS-	90
Naphthalene nucleus	85
-NH-NH-, -O-CO-O-	80
$-NH_2$, -NHR, $-NR_2$	70

Inorganic group	Value
>CO	65
-COOR, -P=P-	60
>C=NH	50
-N=N-	30
>O	20
Benzene nucleus (general aromatic single nucleus)	15
Non-aromatic ring	10
Triple bond	3
Double bond	2

Organic and inorganic group	Organic property value	Inorganic property value
$>SO_2$	40	110
-SCN	70	80
-NCS	70	75
$-NO_2$	70	70
-CN	40	70
-NO	50	50
$-ONO_2$	60	40
-NC	40	40
-NCO	30	30
-I	60	20
-Br, -SH, -S-	40	20
-Cl, -P	20	20

Note: Each carbon atom in the above inorganic groups is counted as 20 in organic property value. However, the values of SO_2 and others are counted in the organic property values of organic and inorganic groups.

EP 0 952 248 A2

[0015] The inorganic property/organic property value of polyethylene terephthalate calculated according to this organic idea is 0.7. In the present invention, attention is paid to the affinity between synthetic fibers and an antimicrobial agent based on the value calculated according to this organic idea, and an antimicrobial agent with the inorganic property/organic property value kept in the predetermined range is infiltrated and diffused in the synthetic fibers.

[0016] If the inorganic property/organic property value is less than 0.3, the organic property is so strong, and if more than 1.4 on the contrary, the inorganic property is so strong that the antimicrobial agent is less likely to be infiltrated and diffused in the synthetic fibers. It is preferable that the inorganic property/organic property value is in a range of 0.35 to 1.3, and a more preferable range is from 0.4 to 1.2.

[0017] For example, 2,3,5,6-tetrachloro-4-hydroxypyridine has an inorganic property value of 265 since it has one benzene nucleus, four -Cl groups, one -OH group and one -NR group, and has an organic property value of 180 since it has five carbon atoms and four -Cl groups. Hence the inorganic property/organic property value of the compound is 1.47. Furthermore, 2-pyridylthiol-1-oxide zinc exists as a chelate complex, and judging from its electronegativity, it is considered that zinc and sulfur form a covalent bond. So, the compound has an inorganic property value of 85 and an organic property value of 190, hence an inorganic property/organic property value of 0.45, according to the calculation method. On the other hand, in the case of 2-pyridylthiol-1-oxide sodium which is also a pyridine based antimicrobial agent, since the electronegativity difference between sodium and sulfur is more than 1.6, the bond is an ionic bond. In this case, sodium acts as a light metal salt. So, the compound has an inorganic property value of 585 and an organic property value of 190, hence an inorganic property/organic property value of 3.0, according to the calculation method. So, it is poor in affinity to polyesters.

[0018] In the present invention, it is preferable that the antimicrobial agent has an average particle size of 2 μm or less. If the average particle size is more than 2 μm, the antimicrobial agent is less likely to be infiltrated and diffused in the synthetic fibers, and when the antimicrobial agent is provided as an aqueous liquid, the particles precipitate, hence the liquid tends to be poor in stability. It is preferable that the average particle size of the antimicrobial agent is 1 μm or less.

[0019] The antimicrobial agents which can be used in the present invention include pyridine based compounds such as 2-chloro-6-trichloromethylpyridine, 2-chloro-4-trichloromethyl-6-methoxypyridine, 2-chloro-4-trichloromethyl-6-(2-furylmethoxy)-pyridine, di(4-chlorophenyl)pyridylmethanol, 2,3,5-trichloro-4-(n-propylsulfonyl)-pyridine, 2-pyridylthiol-1-oxide zinc, and di(2-pyridylthiol-1-oxide). Among them, especially 2-pyridylthio-1-oxide zinc is good in affinity to fibers, and is stably infiltrated in the fibers, being good in washing durability, and is also preferable in view of the variety of strains including MRSA against which it is effective.

[0020] The materials of the synthetic fibers which can be used as the fibrous product of the present invention can be polyesters, acrylic resins, nylons, etc. The fibrous product of the present invention can also be natural fibers of cotton, wool or silk, etc. in addition to those synthetic fibers, or a combination with semi-synthetic fibers such as rayon, as yarns, woven fabric or nonwoven fabric, etc. Among such synthetic fibers, polyester fibers can provide a fibrous product most excellent in the industrial washing durability of antimicrobial activity.

[0021] Furthermore, in the present invention, the fibers can be colored, and it means that fibers contain a colorant such as disperse dye, acid dye, cationic dye or fluorescent whitening agent.

[0022] Considering the antimicrobial activity, a state that the antimicrobial agent is deposited on the surfaces of fibers is most excellent since the frequency of contact with bacteria is high. However, in this state, the antimicrobial agent is likely to be unpreferably removed and, accordingly, the washing durability is not good. On the other hand, if the antimicrobial agent is diffused and forms independent phases of 0.01 μm or more in shorter diameter inside the fibers, washing durability is high though the antimicrobial activity is not so high. Having regard to the washing durability, it is preferable that the size of the antimicrobial agent in the fibers is 0.02 μm or more in shorter diameter. Although a larger size such as 0.5 μm or 1 μm can be effective, the size of the independent phases is preferably 0.02 to 0.5 μm in shorter diameter. Typically, it is 0.02 to 0.2 μm. For these reasons, it can be considered to be excellent in view of both antimicrobial activity and washing durability that the antimicrobial agent is distributed annularly near the surface of each fiber inside the fiber, or diffused like branches from the surface of each fiber into inside, or distributed as lumps here and there inside each fiber.

[0023] The concentration distribution of the antimicrobial agent inside each fiber can be easily confirmed by analyzing a section of the fiber using an X ray microanalyzer (EMAX-2000 produced by Horiba Seisakusho), and evaluating the concentration distribution of any specific element such as sulfur contained in the antimicrobial agent inside the fiber.

[0024] The state where the antimicrobial agent forms independent phases of 0.01 μm or more in shorter diameter inside each fiber, the state where it is distributed annularly near the surface of each fiber, the state where it is diffused like branches from the surface to inside of each fiber inside the fiber, or the state where it is distributed as lumps here and there inside each fiber can be confirmed by observation with a scanning electron microscope (SEM).

[0025] In the present invention, the concentration distribution of the antimicrobial agent inside each fiber can be controlled into several states by changing the processing conditions, into the state where the microbial agent is deposited on the surface of each fiber, into the state where it is distributed annularly in a range from the surface to inside

of each fiber, into the state where it is diffused like branches inside each fiber, or into the state where it is distributed as lumps here and there inside each fiber.

[0026] It is also preferable that the microbiostatic activity value measured according to the microbe control evaluation method (standard testing method) specified by SEK (New Function Evaluation Conference for Fiber Goods) is 2.2 or more still after 50 times of industrial washing treatment of 12 minutes/time at 80°C using a washing liquid containing a surfactant. It is more preferable that the same microbiostatic activity value is maintained even when the washing time was changed to 15 minutes/time.

[0027] It is further more preferable that the microbiostatic activity value is 2.2 or more even if the washing treatment conditions are more severe. That is, it is further more preferable that the same microbiostatic activity value is maintained even when a washing liquid containing a peroxide, strong alkali and surfactant was used. It is most preferable that the same microbiostatic activity value is maintained even when the washing time was changed to 15 minutes/time and the washing liquid containing a peroxide, strong alkali and surfactant was used.

[0028] The washing liquid containing a peroxide, strong alkali and surfactant in this case is prepared, for example, by supplying 2 g/l of detergent "Zab" produced by Kao Corp., 3 cc/l of hydrogen peroxide water (35% industrial use) as a peroxide, and 1.5 g/l of sodium percarbonate as a strong alkali into a drum dyeing machine filled with water at a bath ratio of 1 : 20, and mixing them. The washing liquid is heated to 85°C, and an antimicrobial fibrous product of the present invention and waste cloth are supplied into the liquid, for washing for 15 minutes. The machine is then drained, and the fibrous product is dewatered, washed by water with overflowing for 10 minutes, and finally dewatered. This washing is repeated 50 times, and the fibrous product is dried by a tumbler dryer for 20 minutes, for microbe control evaluation.

[0029] The process for producing the antimicrobial fibrous product of the present invention is described below.

[0030] At first, a fibrous product is immersed in a liquid containing any of said pyridine based antimicrobial agents and a colorant such as a disperse dye, acid dye, cationic dye or fluorescent whitening agent in a jet dyeing machine, and heat-treated at atmospheric pressure or under pressurization at 90 to 160°C. It is preferable that the heat treatment time is 10 to 120 minutes. It is more preferable to heat-treat at 120 to 135°C for 20 to 60 minutes. In this case, since the colorant and the pyridine based antimicrobial agent are heat-treated simultaneously in the liquid, the antimicrobial agent is deposited on the fibers and infiltrated and diffused inside the fibers like the dye. If the pyridine based antimicrobial agent is heat-treated in a bath at 90 to 160°C after the fibrous product has been dyed, the colorant is desorbed from the fibers, not allowing the desired coloring to be achieved. On the other hand, if the fibers containing an antimicrobial agent is colored, the pyridine based antimicrobial agent is desorbed to lower the microbe control performance. If the heat treatment is effected at lower than 90°C, the antimicrobial agent is not infiltrated in the synthetic fibers. If higher than 160°C, the effect obtained is not high enough to be proportional to the energy consumption, thus lowering cost performance.

[0031] It is preferable that the fibrous product treated in the liquid according to the above method is treated by dry heat of 160 to 200°C, using a tenter dryer, etc. The treatment time can be 15 seconds to 5 minutes. It is more preferable that the dry heat treatment is effected at 170 to 190°C for 30 seconds to 2 minutes. The dry heat treatment causes the antimicrobial agent to be diffused inside from the surfaces of the fibers, being distributed annularly inside the fibers, or infiltrated and diffused like chains, to improve the washing durability without impairing the antimicrobial activity. If the heat treatment is effected at lower than 160°C, the effect of dry heat treatment is less likely to be obtained. If higher than 200°C, the fiber material is yellowed or becomes fragile, and the dye and the antimicrobial agent are sublimated or thermally decomposed while energy consumption increases. By changing the treatment conditions, the respective states of adhesion of the antimicrobial agent can be controlled into being deposited on the surfaces of fibers, into annular distribution inside the fibers or into diffusion inside the fibers.

[0032] As another embodiment of the process for producing the antimicrobial fibrous product of the present invention, a liquid containing any of said pyridine based antimicrobial agents is applied to a colored fibrous product by padding or spraying, and the fibrous product is heat-treated in dry or wet state at 160 to 200°C. It is preferable that the heat treatment time is 30 seconds to 10 minutes. It is more preferable that the heat treatment is effected in dry or wet state at 170 to 190°C for 2 to 5 minutes. If the heat treatment temperature is lower than 160°C, the pyridine based antimicrobial agent is not infiltrated in the fibers. If higher than 200°C, the fiber material is yellowed or becomes fragile and the dye and the antimicrobial agent are sublimated or thermally decomposed while the energy consumption increases.

[0033] It is preferable that the pyridine based antimicrobial agent is granulated in a colloidal state. If the antimicrobial agent is colloidal, it can be stably infiltrated and diffused in the fibers. Especially if it is made colloidal by water and a formalin condensation product, the antimicrobial agent becomes higher in dispersibility and can keep a good dispersed state, being good in affinity to the synthetic fibers.

Examples

[0034] The present invention is described below more concretely in reference to examples. The "%" and "parts" in

the examples are "wt%" and "parts by weight" unless otherwise stated. The quality evaluation in the examples was effected according to the following methods.

(1) Washing method

[0035] A fibrous product was washed in a drum dyeing machine containing 2 g/l of detergent "Zab" produced by Kao Corp., 3 cc/l of hydrogen peroxide water (35% industrial use) and 1.5 g/l of sodium percarbonate at 85 ± 2°C at a bath ratio of 1 : 20 for 15 minutes, and the machine was drained. The fibrous product was dewatered, washed by water with overflowing for 10 minutes and dewatered. This washing was repeated. Finally, the fibrous product was dried using a tumbler dryer for 20 minutes.

(2) Antimicrobial activity testing method

[0036] The standard testing method was adopted, and a clinically isolated MRSA strain was used. A bouillon suspension of said test strain was injected into a cloth sample, and cultured in a sealed container at 37°C for 18 hours. The viable cell number in the sample was counted, and the decrement or increment from the planted viable cell number was obtained, to judge according to the following criterion.

[0037] When the decrement or increment expressed by log(B/C) at log(B/A) > 1.5 was 2.2 or more, the antimicrobial activity was judged to be acceptable.

[0038] In the above formulae, A denotes the viable cell number of the strain obtained by diffusing and collecting it from a sample not treated by any antimicrobial agent immediately after inoculating the sample with the strain; B denotes the viable cell number of the strain obtained by diffusing and collecting it from a sample not treated by any antimicrobial agent after culturing the strain in the sample for 18 hours; and C denotes the viable cell number of the strain obtained by diffusing and collecting it from a sample treated by an antimicrobial agent after culturing the strain in the sample for 18 hours.

(3) Distribution of antimicrobial agent inside fibers

(3-1) Confirmation of concentration distribution

[0039] A section of a fiber was analyzed using an X-ray microanalyzer (EMAX-2000 produced by Horiba Seisakusho), and with attention paid to any specific element such as sulfur contained in the antimicrobial agent, the concentration distribution of the antimicrobial agent inside the fiber was evaluated.

(3-2) Confirmation of infiltration and diffusion

[0040] The deposition of an antimicrobial agent on the surface of a synthetic fiber, or the annular distribution of it inside a synthetic fiber, or the state where it branched to diffuse inside from the surface of a fiber, or the state where it was distributed as lumps here and there was confirmed by observation with a scanning electron microscope (SEM).

[0041] Examples 1 to 4, and Comparative Examples 1 to 4 were conducted according to the following conditions.

[0042] The antimicrobial agents used in the examples and comparative examples were treated to be colloidal. That is, 50 g of the antimicrobial agent used in any of the examples, 20 g of formalin condensation product of naphthalenesulfonic acid and 30 g of sodium lignosulfonate were formed into a slurry together with 300 g of water, and the slurry was wet-ground using glass beads, to obtain a colloidal composition with an average particle size of 1 μm

[0043] A cloth sample used was prepared as follows. The polyethylene terephthalate filament yarns described below were used to prepare a tubular knitted fabric using a circular knitting machine.

[0044] A cloth sample was made antimicrobial according to the following method. A cloth sample was immersed in a liquid containing 1% owf of an antimicrobial agent made colloidal according to the above method, 2% owf of a disperse dye and 0.5 g/l of a level dyeing agent at a bath ratio of 1 : 10 and pH 5 and dyed at 130°C for 60 minutes according to a conventional method using a high pressure dyeing tester. It was washed by water and dried at 170°C for 2 minutes, to obtain an antimicrobial cloth sample.

[0045] The cloth samples and antimicrobial agents used in the respective examples and comparative examples are stated below.

Example 1

[0046] A knitted fabric of drawn 75-denier 72-filament polyethylene terephthalate yarns was used as the cloth sample, and 2-pyridylthiol-1-oxide zinc was used as the antimicrobial agent. The antimicrobial agent had an average particle

size of 2 μm, and in the cloth treated by it, it was partially deposited on the surfaces of fibers and mostly infiltrated or branched to diffuse inside from the surfaces of fibers, mostly being distributed near the surface layers.

Example 2

[0047] A knitted fabric of falsely twisted 150-denier 48-filament polyethylene terephthalate yarns was used as the cloth sample, and 2-pyridylthiol-1-oxide zinc was used as the antimicrobial agent. The antimicrobial agent had an average particle size of 0.5 μm, and in the cloth treated by it, it was partially deposited on the surfaces of the fibers and mostly branched to diffuse inside the fibers, the branches being distributed to near the centers of the sections.

Example 3

[0048] A knitted fabric of falsely twisted 75-denier 12-filament polyethylene terephthalate yarns was used as the cloth sample, and 2-chloro-6-trichloromethylpyridine was used as the antimicrobial agent. The antimicrobial agent had an average particle size of 1 μm, and in the cloth treated by it, it was partially deposited on the surfaces of the fibers and mostly branched to diffuse inside the fibers, the branches being distributed to near the centers of the sections.

Example 4

[0049] A knitted fabric of falsely twisted 150-denier 48-filament polyethylene terephthalate yarns was used as the cloth sample, and 2-chloro-4-trichloromethyl-6-(2-furylmethoxy)pyridine was used as the antimicrobial agent. The antimicrobial agent had an average particle size of 0.5 μm, and in the cloth treated by it, it was partially deposited on the surfaces of fibers and mostly branched to diffuse inside the fibers, the branches being distributed near to the centers of the sections.

Comparative Example 1

[0050] A cloth sample was treated as described in Example 1, except that the average particle size of the antimicrobial agent was changed to 3 μm.

Comparative Example 2

[0051] A cloth sample was treated as described in Example 1, except that the dyeing (treatment) temperature was changed to 85°C.

Comparative Example 3

[0052] A cloth sample was treated as described in Example 2, except that the antimicrobial agent was changed to 2-pyridinethiol-1-oxide sodium.

Comparative Example 4

[0053] A cloth sample was treated as described in Example 2, except that the antimicrobial agent was changed to 1,4-(1-diiodomethysulfonyl) benzene.

[0054] Examples 5 and 6 and Comparative Examples 5 and 6 were conducted according to the following conditions.

[0055] The same cloth sample as Example 1 was dyed with a disperse dye. And, to make the pre-dyed cloth sample antimicrobial, it was immersed in an aqueous liquid containing 15 g/l of any of the following antimicrobial agents made colloidal according to the above method, squeezed to 70 wt% of the solution based on the cloth weight by a mangle, dried by a tenter dryer at 120°C for 2 minutes, and heated at 190°C for 1 minute.

Example 5

[0056] A knitted fabric of 100-denier 48-filament polyethylene terephthalate yarns was used as the cloth sample, and 2-pyridylthiol-1-oxide zinc was used as the antimicrobial agent. The antimicrobial agent had an average particle size of 2 μm, and in the cloth treated by it, it was partially deposited on the surfaces of fibers and mostly infiltrated to be distributed annularly.

Example 6

[0057] A sample cloth was treated as described in Example 7, except that the average particle size of the antimicrobial agent was 0.5 μm. In the cloth treated by the antimicrobial agent, it was partially deposited on the surfaces of fibers and mostly infiltrated to be distributed as lumps here and there.

Comparative Example 5

[0058] A sample cloth was treated as described in Example 5, except that the antimicrobial agent was changed to methyl-6-(2-thiophenecarbonyl)-1H-2-benz-imidazolecarbamate.

Comparative Example 6

[0059] A sample cloth was treated as described in Example 6, except that the antimicrobial agent was changed to 5-chloro-2-methyl-4-isothiazoline.

[0060] Six samples of the examples and six samples of the comparative examples, total 12 samples, were evaluated on antimicrobial activity (MRSA) before washing and after 50 times of industrial washing. The results are shown in Table 2.

[0061] As can be seen from Table 2, the samples of Examples 1 to 8 had sufficient antimicrobial activity before washing and also after 50 times of industrial washing. On the other hand, the samples of Comparative Examples 1 to 8 did not show any effect after 50 times of industrial washing, though some showed an antimicrobial effect before washing. As described above, the present invention can provide a fibrous structure having antimicrobial activity with excellent industrial washing durability and a production process thereof.

Table 2

		Antimicrobial agent		
		Name (molecular weight)	Average particle size*1	Inorganic/ organic*2
Examples	1	2-pyridylthiol-1-oxide zinc (317)	2 μm	0.45
	2		0.5 μm	
	3	2-chloro-6-trichloromethylpyridine (219)	1 μm	0.83
	4	2-chloro-4-trichloromethyl-6-(2-furylmethoxy)pyridine (329)	0.5 μm	0.73
	5	2-pyridylthiol-1-oxide zinc (317)	2 μm	0.45
	6		0.5 μm	
Comparative Examples	1	2-pyridylthiol-1-oxide zinc (317)	3 μm	0.45
	2		0.5 μm	
	3	2-pyridylthiol-1-oxide sodium (149)	3 μm	3.00
	4	1,4-(1-diiodo-methylsulfonyl)benzene (738)	2 μm	0.66
	5	Methyl 6-(2-thiophenecarbonyl)-1H-2-benzimidazolecarbamate (302)	0.5 μm	1.52
	6	5-chloro-2-methyl-4-isothiazoline-3-one (150)	0.5 μm	1.34

*1: Number average
*2: inorganic property/organic property value
*3: Symultaneously with dyeing
*4: Based on fiber weight and determined by HPLC ana
*5: Number average
*6: 2.2 or more after washing is acceptable

Table 2 (continued)

Treating conditions		Infiltrated and diffused state c	
method	Temp.	Infiltrated amount (wt%)*4	State
In a dyeing bath*3	130℃	0.10	Branched to diffuse from the surfaces to inside of fibers, being mainly distributed near the surface layers.
		0.40	Branched to diffuse from the surfaces to inside of fibers, the branches being distributed to the centers.
		-	
		-	
Padding and curing	180℃	0.15	Annularly distributed.
		0.18	Distributed as lumps here and there.
In a dyeing bath	130℃	0.03	Deposited on the surfaces of fibers, but little infiltrated inside the fibers. After industrial washing, the antimicrobial agent in the surface layers mostly fell off
	85℃	< 0.01	
	130℃	< 0.01	
		-	
Padding and curing	180℃	-	
		-	

alysis after cabonization

Table 2 (further continued)

of antimicrobial agent in fibers					Microbiostatic activity value*6
Concentration gradient ratio	Diffusion degree	Shorter diameter*5	Percentage of depth		
			1 μm or more	2 μm or more	
1:2	0.3	0.15	80%	40%	4.6(○)
1:4	0.4	0.12	75%	40%	5.0(○)
1:5	0.4	0.13	80%	55%	4.8(○)
1:5	0.5	0.14	70%	50%	5.0(○)
1:7	0.8	0.15	70%	45%	5.7(○)
1:8	0.9	0.15	65%	35%	5.8(○)
1:2	0.1	unclear	30%	20%	1.8(×)
1:1	0.05	No independent phase was observed	20%	5%	1.0(×)
1:2	0.2		40%	25%	1.2(×)
1:1	0.05		15%	10%	1.8(×)
1:1	0.2		30%	20%	1.0(×)
1:3	0.1		35%	15%	1.9(×)

Claims

1. A molded antimicrobial article comprising an infiltrated antimicrobial agent which forms independent phases of 0.01μm or more in shorter diameter in the molded article.

2. A molded antimicrobial article according to claim 1 wherein the antimicrobial agent is pyridine based.

3. A molded antimicrobial article according to claim 1 or 2 wherein the antimicrobial agent has an inorganic property/ organic property value of 0.3 to 1.4.

4. A molded antimicrobial article according to claim 1, 2 or 3 wherein the molecular weight of the antimicrobial agent is 200 to 700.

5. A molded antimicrobial article according to any preceding claim wherein the molded article is a fibre.

6. A molded antimicrobial article according to any preceding claim wherein 50% or more of the antimicrobial agent is infiltrated in a depth range of lμm or more from the surface of the molded article.

7. A molded antimicrobial article according to any preceding claim wherein 30% or more of the antimicrobial agent is infiltrated in a depth range of 2μm or more from the surface of the molded article.

8. A molded antimicrobial article according to any preceding claim wherein the pyridine based antimicrobial agent is at least one selected from 2-chloro-6-trichloromethyl-pyridine, 2-chloro-4-trichloromethyl-6-methoxypyridine, 2-chloro-4-trichloromethyl-6-(2-furylmethoxy)pyridine, di (4-chlorophenyl)pyridyl-methanol, 2,3,5-trichloro-4-(n-propylsulfonyl)pyridine, 2-pyridylthiol-1-oxide zinc and di(2-pyridylthiol-1-oxide).

9. A molded antimicrobial article according to any preceding claim wherein the pyridine based antimicrobial agent is 2-pyridylthiol-1-oxide zinc.

10. A molded antimicrobial article according to claim 5 wherein the pyridine based antimicrobial agent is infiltrated in a synthetic fibre.

11. A molded antimicrobial article according to claim 10 wherein the synthetic fibre is a polyester.

12. A molded antimicrobial article according to claim 10 or 11 wherein the synthetic fibre is colored by a disperse dye.

13. A molded antimicrobial article according to claim 10 or 11 wherein the synthetic fibre is colored by an acid dye.

14. A molded antimicrobial article according to claim 10 or 11 wherein the synthetic fibre is colored by a cationic dye.

15. A molded antimicrobial article according to claim 10 wherein the pyridine based antimicrobial agent is distributed annularly near the surfaces of the synthetic fibre inside the fibre.

16. A molded antimicrobial article according to claim 10 wherein the pyridine based antimicrobial agent is diffused to form branches extending from the surface to inside of the synthetic fibre inside the fibre.

17. A molded antimicrobial article according to claim 1 wherein the microbiostatic activity value measured according to the microbe control evaluation method (standard testing method) specified by SEK (New Function Evaluation Conference for Fibre Goods) is 2.2 or more still after industrial washing of 12 minutes/time at 80°C x 50 times by a washing liquid containing a surfactant.

18. A process for producing a molded antimicrobial article comprising the steps of immersing a molded resin article in a liquid containing a pyridine based antimicrobial agent with a molecular weight of 200 to 700, an inorganic property/organic property value of 0.3 to 1.4 and an average particle size of 2μm or less, and a colorant, and heat-treating at 90 to 160°C.

19. A process for producing a molded antimicrobial article according to claim 18 wherein dry heat treatment is effected at 160 to 200°C after the heat-treatment in the aqueous liquid.

20. A process for producing a molded antimicrobial article comprising the steps of applying a pyridine based antimicrobial agent with a molecular weight of 200 to 700, an inorganic property/organic property value of 0.3 to 1.4 and an average particle size of 2μm or less to a molded resin article by padding or spraying, and heat-treating it at 160 to 200°C in dry or wet state.

21. A process for producing a molded antimicrobial article according to claim 18 wherein the pyridine based antimicrobial agent is granulated in a colloidal state.

22. A process for producing a molded antimicrobial article according to claim 21 wherein the pyridine based antimicrobial agent is made colloidal by water and a formalin condensation product.